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Fouling in Heat Exchangers

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Abstract

A major problem in industries that use heat exchanger equipment cooled with water in their industrial processes is biofouling. In the design and operation of heat exchangers cooled with water, a coefficient of biological must be considered, which affects the efficiency of the equipment. For this reason, it is necessary to apply appropriate antifouling treatments to the design of each heat exchanger. In order to minimize the undesirable phenomenon of biofouling, various mitigation methods have been developed over the last 30 years, both online and offline, of a physical, chemical, or biological nature. Most of these methods are well contrasted and are applied in the regular operation of the facilities, although some methodology approaches are in the research and development phase. However, the application of most of these methods requires interrupting the production, periodically, in order to clean the biofouling, seriously damaging the performance and operation of the installation. The “online” methods to biofouling control are chemical (oxidizing, and non-oxidants), biological and physical treatments. Nowadays, other methodologies of biofouling mitigation that do not affect the environment are being investigated, although, until now, none have been found that are substitutes for chemical agents and that have the same or with higher efficiency.

Keywords: biofouling, biofilm, fouling, antifouling, energy, efficiency

1. Introduction

A major problem in industries that use heat exchange equipment cooled with seawater in their industrial processes is biological fouling (biofouling) (**Figure 1**). Biofouling acquires greater relevance when it develops in the marine environment, due to the high biological activity of seawater [1]. In the design and operation of heat exchangers cooled with seawater, a biological fouling coefficient must be considered, which affects the efficiency of the equipment [2]. For this reason, it is necessary to apply appropriate antifouling treatments to the design of each heat exchanger [3].

In order to minimize the undesirable phenomenon of biofouling, various mitigation methods have been developed over the last 30 years, both online and offline, of a physical, chemical, or biological nature. Most of these methods are well contrasted and are applied in the regular operation of the facilities, although some methodology approaches are in the research and development phase. However, the application of most of these methods requires interrupting production, periodically, in order to proceed with biofouling cleaning, as this seriously impairs the performance and operation of the facility (**Figure 2**).

Oxidizing chemical methods are available [4] and non-oxidants [5], biological [6–8] for “on-line biofouling control. Nowadays, other methodologies of biofouling mitigation that do not affect the marine environment are being investigated [3],



Figure 1.
Presence of mussels in the water box of a condenser (Source: By courtesy of Nuclenor).



Figure 2.
Tubular heat exchanger in maintenance due to the presence of biofouling in its tubular bundle (Source: By courtesy of Merus-the water conditioner company).

although, until now, none have been found that are substitutes for chemical agents and that have the same or with higher efficiency.

Other “offline” methods, such as antifouling coatings (AF) or mechanical cleaning, are widely used in heat exchangers. AF coatings have the drawback of using chemicals that can harm the environment. Nowadays, new coatings are being researched to avoid the growth of biofouling, without harming the environment [9, 10].

2. Classification of the fouling

For a better understanding of the biofouling problem, this chapter begins with the description of the general term “fouling” and its types, among which is biofouling. This term is used to define the accumulation of biotic and/or abiotic deposits on a surface in contact with a fluid. This type of soiling can occur in nature in many different ways and is usually classified in the following categories [11]:

- Biological fouling
- Fouling by chemical reaction
- Fouling by corrosion

- Ice-cold fouling
- Fouling by precipitation
- Fouling by particles

2.1 Biological fouling

The biological fouling or biofouling in the Anglo-Saxon literature depends on the material on which the accumulation of macrofouling or microbial biofouling occurs, which originates from microfouling or microbial biofouling.

2.2 Fouling by chemical reaction

Deposits caused by chemical reaction can be initiated by the contact of two chemicals in a heat transfer process. In some cases, the metal surface favors precipitation by acting as a catalyst.

This type of fouling is frequently observed in the petroleum industry, in which the refining processes induce the polymerization of unsaturated hydrocarbons (**Figure 3**).

2.3 Fouling by corrosion

This type of fouling occurs as a result of electrochemical or microbial corrosion of a surface in contact with a fluid (**Figure 4**). The composition of corrosion products is normally a function of the material from which they originate. According to [12] corrosion must be taken into account in the design of heat exchangers in order to generate more information on the thermal resistance associated with fouling by corrosion.

2.4 Freezing fouling

It is the accumulation of solid deposits on a refrigerated surface due to the solidification of a fluid or one of its constituents. The accumulation of this type of fouling depends on the temperature of the surface and the shearing effect produced by the fluid on the surface as a function of its velocity of circulation [13, 14]. This phenomenon is seen in the solidification of the wax, whose melting point is high, in a hydrocarbon solution on a heat exchange surface (**Figure 5**).



Figure 3.
Residue of hydrocarbon in the tubes of a heat exchanger (Source: By courtesy of H&C Heat Transfer Solutions Inc. 2013).



Figure 4.
Oxides of corrosion in the tubes of a heat exchanger (H&C Heat Transfer Solutions Inc. 2013).



Figure 5.
Icy icing of polymer products in a heat exchanger (Source: By courtesy of H&C Heat Transfer Solutions In.).

2.5 Fouling by precipitation

The origin of this type of fouling is the precipitation or scaling of dissolved substances on the surfaces. Precipitation usually occurs from aqueous solutions based on their temperature and the solubility of dissolved substances, such as calcium carbonate (CaCO_3), whose precipitation of the solution occurs on a superheated surface when the water contained in the water evaporates (**Figure 6**).

The precipitation of the salts dissolved in the water originates when coming into contact with the wall of the hot tube and supersaturation occurs. The deposits adhered to the surface may have different hardness depending on their composition. Thus, when the deposit is only composed of salts, it is hard and very adherent. On the other hand, if the deposit is a mixture of salts and suspended solids, its hardness is low, and they adhere weakly [15].

The precipitates usually observed in industrial facilities that use aqueous solutions are the following [16]:

- Calcium carbonate
- Calcium sulfate
- Calcium oxalate
- Barium sulfate
- Magnesium hydroxide
- Silicates
- Aluminum oxides
- Aluminum silicate
- Copper
- Phosphates
- Magnetite

These precipitates are very common in boilers and heat exchangers that operate with water of high hardness.

2.6 Fouling by particles

It is the accumulation of solid particles that are suspended in a fluid (liquid or gas). The particles are deposited on surfaces by means of various mechanisms, some of which are closely linked to properties of particles as specific as coagulation. The amount of deposit and the rate of accumulation on the surfaces depend on the size and nature of the particles, as well as the environmental conditions. When gravity is the main mechanism of deposition of suspended particles on a surface, fouling is called sedimentation (**Figure 7**) [17].



Figure 6.

Precipitated salts in the tubes of a heat exchanger (Source: By courtesy of H&C Heat Transfer Solutions Inc).



Figure 7. Accumulation of solid particles in the plate of a tubular heat exchanger (Source: By courtesy of AH&C Heat Transfer Solutions Inc.).

3. Biofouling

The term biofouling is clearly defined and accepted by the scientific community, although in the various definitions proposed by different authors some aspects of others are highlighted, depending on the importance given by each author to the different facets of the phenomenon. Below are several definitions of this term, published over the past years by different authors:

- Biofouling is simply the union of an organism or organisms to a surface in contact with water over a period of time [18].
- Biofouling is the colonization of submerged surfaces, produced by unwanted organisms such as bacteria, algae, and barnacles. Biofouling has detrimental effects on transport and leisure vessels, heat exchangers, oceanographic sensors, and aquaculture systems [19].
- Biofouling can be defined as the union and growth of a community of plants and animals [20].
- Biofouling is defined as the fixation and growth of organisms on submerged surfaces of an artificial nature. The accumulation of biofouling includes barnacles and other sessile marine invertebrates [21].
- Biofouling is the unwanted accumulation of microorganisms, algae, arthropods, or mollusks on a surface [18].

The definition of the term biofouling accepted is the following: “biofouling can be defined as the undesirable phenomenon of adhesion and accumulation of biotic deposits on an artificial surface submerged or in contact with seawater.” This accumulation or embedding consists of an organic film composed of microorganisms embedded in a polymer matrix created by themselves (biofilm), where they can reach and retain inorganic particles (salts and/or corrosion products) as a result of other types of fouling developed in the process. This biofilm composed of

microorganisms (microbial biofouling or microfouling) can lead to the accumulation of macroorganisms (macrobial biofouling or macrofouling) [22].

3.1 Evolution of the research of biofouling

Zobell [23] examined a natural marine population through a direct microscope and observed that the number of bacteria adhered to the surfaces was much higher than that found in the medium. In addition, these bacteria were characterized by showing an activity and high growth rates, concluding that the bacteria were attracted to the surfaces to which they adhered to form sessile populations.

The first detailed examination of the nature and composition of the biofilm had to wait for the appearance of the electron microscope, which provided a greater extension with respect to optical microscopy and, in its scanning and transmission modalities, was able to show the variety of microorganisms that made up the biofilm in a treatment plant [24]. Staining the biofilm with ruthenium red and fixing it with osmium tetroxide allowed to show that the material that surrounds and encloses the cells that compose it is composed mainly of polysaccharides. Costerton et al. [25], taking as a starting point the observations of sessile communities in the mountain streams, elaborated a theory that explains the mechanisms through which microorganisms adhere to living or inert materials, as well as the benefits obtained for their ecological niche. From this moment, numerous studies of the biofilm were developed in both industrial and ecological scenarios [26].

The possible effects of the biofilm in industrial processes are derived from the beneficial or harmful reactions that can be carried out by the microorganisms that compose it and that depend on the environmental conditions of the environment. These conditions have a great influence on the growth and metabolic activity of the biofilm [27].

The bacteria that make up the biofouling can be up to a thousand times more resistant to antibiotics than the same bacteria grown in a controlled liquid medium. The mechanisms responsible for this resistance include (1) the physical and chemical diffusion barrier that constitutes the matrix of the biofilm to the penetration of antimicrobials, (2) the slowed growth of biofilm bacteria due to nutrient limitation, (3) the existence of microenvironments that antagonize the action of the antibiotic, and (4) the activation of stress responses, which cause changes in the physiology of the bacteria and the appearance of a specific biofilm phenotype that actively combats the negative effects of antimicrobial substances [28]. Due to this resistance, antifouling substances must be highly effective and incorporated at considerably high concentrations, which can lead to harmful effects on the environment.

3.2 Microfouling

The biofilm (microfouling) is composed mainly of water, in intervals that are between 87 and 99% of the total content. The rest of the components is very variable depending on the medium in which it is studied [17]. The matrix of the biofilm is a complex formed mainly by exopolysaccharides and bacterial cells. Other compounds that can be found are macromolecules such as proteins, DNA, and various products derived from the destruction of the cell wall of bacteria [29].

3.2.1 Development of the biofilm

The biofilm begins to be generated when an individual cell initially joins a surface. The ability of this cell to carry out this binding and initiate cell growth depends on factors such as temperature and pH of the medium, genetic factors that

encode its motor functions and environmental sensitivity, and those that generate adhesins and other proteins [30–33]. The factors that directly affect its development depend mainly on the microbial species, although a part of these characteristics is common to numerous bacteria.

Once initial biofouling adhesion is produced, cell growth and expansion begin on the surface, forming monolayer microcolonies. At the same time, the cells modify their activity and begin the complex process of structure formation of the biofilm. The most obvious of these changes is the production of the exopolymer matrix (EPS), which will unite the whole [34]. If the conditions of the medium allow it, the biofilm will grow and spread to non-colonized areas releasing cells that will be distributed through the water in search of new surfaces to colonize.

The formation of the biofilm is a systematic process of predictable evolution, in which five phases are differentiated [35]: (1) the reversible adsorption of the bacterium to the surface, (2) the irreversible union, (3) the first maturation phase with growth and division, (4) the growth phase with production of the exopolymer, and (5) the final development of the colony with dispersion of colonizing cells (**Figure 8**).

3.2.2 Conditioning of the surface

The ability to bind to different materials depends on the specific proteins of its coat and the bacterial motor appendages. According to Pedersen [36], stainless steel can be as susceptible to the formation of biofilms as plastic. This is because the organic matter present in the water previously comes in contact with the surface, depositing an organic layer in the water/surface interface that changes the chemical and physical properties of the surface, improving the possibilities of fixing the bacteria.

3.2.3 Adsorption of molecules

The adsorption of ions and other dissolved substances (sugars, amino acids, proteins, fatty acids, etc.) begins when the material submerges under seawater

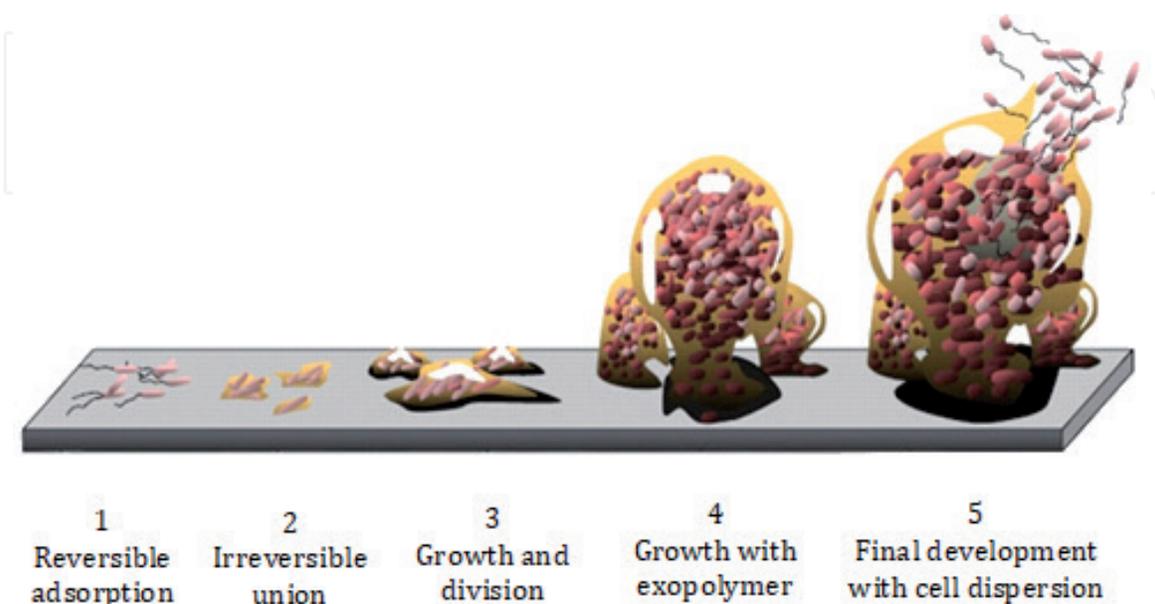


Figure 8. Phases of biofilm formation (Source: By courtesy of Center Biofouling Engineering).

and accelerates when the fluid begins to circulate through the heat exchanger. This adsorption occurs rapidly on the surface, saturating the concentration of substances on the surface in a few minutes [37].

3.2.4 Adhesion of microorganisms

The adhesion of microorganisms to a substrate can be active (by flagella, fimbrias, adhesins, capsules, and surface charges) or passive (by gravity, diffusion, and fluid dynamics). In the absence of these mechanisms, the bacterial cells would be repelled by the surface when presenting electric charges of the same sign [38].

In a few minutes, the free bacteria form a reversible EPS matrix with the “conditioned” surface (**Figure 9**) [39], whose characteristics depend on the electrical charges of the bacteria. These attractive forces have their origin in hydrogen bonds, cation bonds, and van der Waals forces that compete with the forces of repulsion. If this union is maintained long enough, new chemical and physical structures appear that make it permanent and irreversible [40].

In cases of high microbial population density or lack of nutrients in the water, some microorganisms are able to individually alter their cell wall to make it more hydrophobic and increase its greater affinity of adhesion toward the surfaces. When the microorganisms approach the surface, with almost no water flow, they are attracted, proving their affinity for union and fixation (**Figure 10**) [41].

During the reversible adsorption stage, the bacterial cells still show Brownian motion and are easily removed with a nonaggressive cleaning method. The irreversible union implies the anchoring of bacterial appendages and the production of exopolymers, which determines that the mechanical action necessary to detach them will be greater depending on the time that the biofilm is active.

Bacteria undergo important transformations in their structure to adapt to the environment. These transformations activate different genes that encode new structural proteins and enzymes, which explains the adhesion and resistance of biofilm bacteria to antibiotics and disinfectants. In recent years, the advances made in the field of proteomics and genomics have allowed the identification of 800 proteins that modify their concentration throughout the five phases of the biofilm development and clarify the complex process of biofilm formation [42, 43].

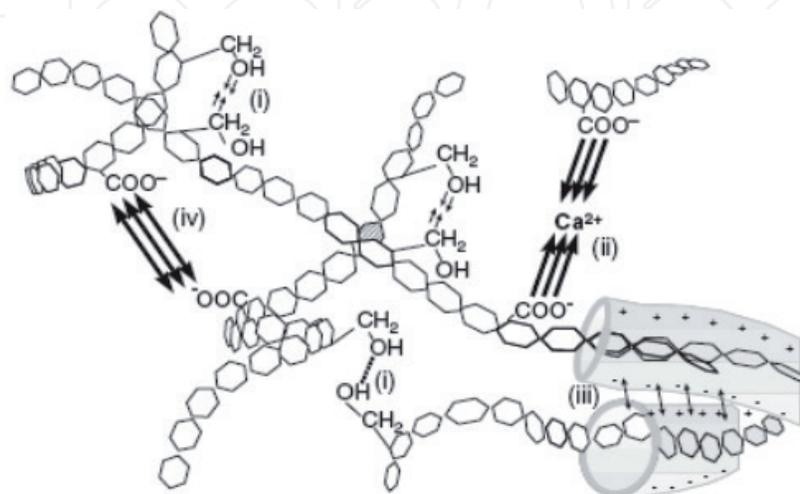


Figure 9.
Binding forces in an EPS matrix: (i) hydrogen bonds, (ii) cation bonds, (iii) van der Waals forces and (iv) repulsion force [38].

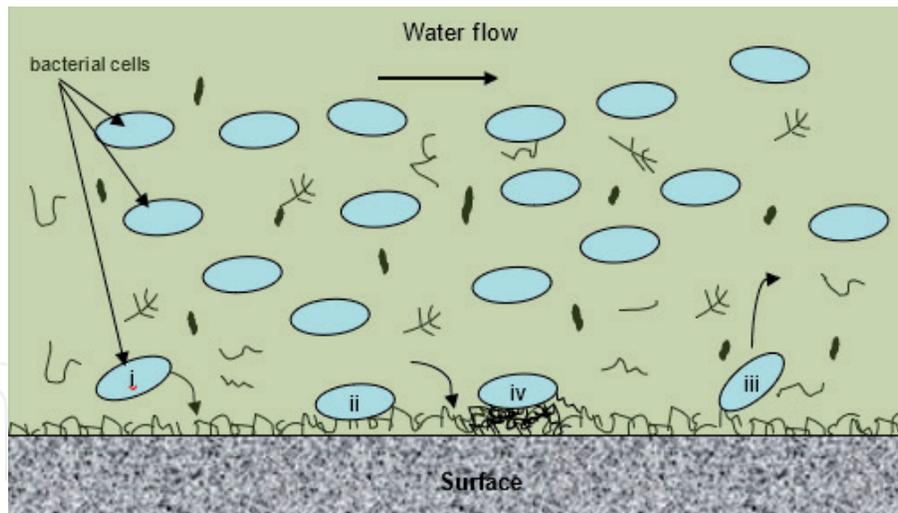


Figure 10. Water flow transport of a bacterial cell to the conditioned surface: (i) adsorption, (ii) reversible adsorption, (iii) detachment and (iv) irreversible adsorption [40].

3.2.5 Maturation

Environmental stability favors biofouling growth and multiplication of cells which allows to generate a polyanionic polymer mixture of silty and sticky consistency whose are excreted to the outside to facilitate union cells onto surface.

Although its composition is not completely known, the mixture of exopolymers is formed by polysaccharides or glycoproteins of various sugars (glucose, fructose, mannose, N-acetylglucosamine, and others) [44] and, additionally, may contain free proteins, phospholipids, and nucleic or teichoic acids [45]. These free proteins are useful for retaining nutrients and protecting bacteria from various biocides.

Extracellular exopolymeric material or glycocalyx is expelled from the bacterial cell wall and adopts a reticular structure reminiscent of a spider. This structure is formed from groups of polysaccharides both neutral and carriers of electric charges, which act as ion exchange systems, capable of capturing and concentrating the nutrients present in the medium.

The structure of the biofilm interacts in a complex way, showing a behavior similar to that of multicellular organisms. If a microorganism generates toxic waste, another will use it as food and, in this way, coordinate the biochemical resources of all the beings that inhabit the matrix of the biofilm. In addition, some bacteria clump together within the matrix with a series of enzymes that allow them to digest nutrients that no isolated species could digest. Also, these enzymes will be used to respond to the attack of various biocides.

Anaerobic biofilms can be developed under the aerobic layer whose structure is permeabilized with a mesh of furrows crossed by water, bacterial debris, enzymes, nutrients, metabolites and oxygen. The gradients of ions and molecules that are established between the different zones generate the necessary impulse to take the substances to the periphery of the biofilm where most of the cells are located. The number of these cells is reduced with the age of the biofilm, being 80% in a young matrix and 50% in an aged shade [42].

3.2.6 Growth and dispersion

Biofilm formation has continuous divisions of the cellular matrix colony, which means a periodic detachment of groups of cells that deposit downstream.

These new colonies take advantage of the release of residues and nutrients from the original colonies to prepare the new surface and to feed other cells, and, as a consequence, the new colonies will grow and spread much more rapidly than in the original biofilm. This colonization is related to the long-term evolution and survival of bacteria [30].

If the conditions of the fluid allow it, the equilibrium that is established between the growth of the colony and the movement of the water releases few cells (**Figure 11**). With an intense or turbulent flow, many more can be released, even releasing whole areas of the biofilm colony.

3.2.7 Contribution of nutrients to the biofilm

The main factor controlling the growth of the biofilm is the availability of dissolved nutrients and their conversion into accumulated biomass. In cooling water circulation systems, the transfer of nutrients to the biofilm tends to increase with flow velocity [41]. Also, the rough surfaces of biofilms increase the transfer of nutrients about three times in relation to smooth surfaces [30, 46]. The control of nutrients is a way to control the development of the biofilm [47–49]. Melo and Bott [50] observed, in an industrial refrigeration system, an increase of 400% in the thickness of the biofilm at a speed of 1.2 ms^{-1} for an increase in the nutrient level of 4 mg L^{-1} at 10 mg L^{-1} .

The chemical composition of the waters determines the number, diversity, metabolic state of the bacteria, and their tendency to adhere to surfaces [51]. So far there has been no study that directly relates nutrients, biofilms, and colonization. Huang et al. [52] demonstrated in the laboratory that the availability of nutrients and the synthesis of new proteins for the formation of biofilms of *Pseudoalteromonas spongiae* under static conditions and without added nutrients affected the induction and adhesion of the biofilm to the surface. The effects of organic substances in the form of amino acids on the bioactivity of the biofilm were studied by Jin and Qian [53, 54]. The results of this study showed that the incorporation of aspartic acid and glutamic acid causes a significant increase in the bacterial mass, modifies its structure, and increases the inducing effect of biofilm formation. In addition, Huang et al. [55] found that the characteristics of biofilms generated in habitats with different environmental conditions show remarkable differences in the bioactivity of the larval settlements of the barnacle, which

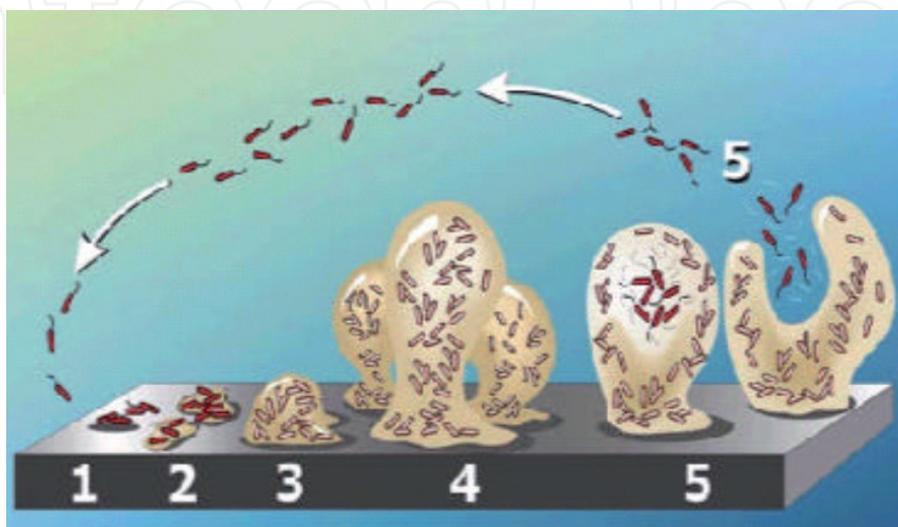


Figure 11. Microbial cell transport during the growth phases of the biofilm (Source: By courtesy of Center Biofouling Engineering).

suggests that the nature of the nutrients is a determining factor of the biological activity in the biofilm.

The nutrients required by microorganisms for feeding are divided into two broad categories [56]:

- Macronutrients (C, H, O, N, P, S, K, Mg)
- Micronutrients or trace elements (Co, Cu, Zn, Mo, etc.)

In nature, these elements are combined as part of organic and inorganic substances. Some of the nutrients will be incorporated to build macromolecules and cellular structures; others only serve for energy production not directly incorporated as cellular material, and others can perform both functions [56].

The bacterial colony exhibits a great metabolic versatility in the use of nutrients. Autotroph bacteria obtain their carbon by reducing CO₂ and other elements from inorganic sources. On the other hand, heterotroph bacteria use to wide ranges of organic carbon sources. In turn, within the heterotrophs, you can find many and varied types of nutrition, from methylotrophic bacteria that only use methane or methanol as carbon and energy sources to the very versatile *Pseudomonas*, which can resort to degrade more than 100 types of carbon sources (including aliphatic and cyclic hydrocarbons). In any case, among the heterotrophs, the most widespread source of carbon is glucose [56].

3.2.8 Abiotic and biotic factors that influence the development of the biofilm

Alterations in the structure of biofilms can be caused by abiotic factors such as [30]:

- Depth.
- Illumination.
- Exhibition time.
- Height of the tides.
- Water circulation regime.
- Physical alteration.
- Latitude.
- Season.
- Water chemistry.
- Supply of nutrients.
- Physical and chemical (abiotic) conditions at the seawater/biofilm interface are an important factor for the development of the biofilm. As the thickness of the biofilm increases, variations in pH, dissolved oxygen, and metabolic by-products are more important and generally directly influence its development [57].

The biotic factors that can alter the structure of the biofilm are [40]:

- Availability and physiological state of organisms, interaction between organisms, and biological disturbances [58–60]
- Properties of adhesion of microorganisms under conditions of turbulence.
- Physiological state of the organisms that have a selective advantage for the formation and development of the biofilm [61]. This capacity is reinforced by the secretion of EPS that are more resistant to high flow rates and chemical agents [62]. Microorganisms in the biofilm are released when conditions become unfavorable [63].

3.3 Effects produced by biofouling in heat exchangers

Biofouling has a great influence on the thermal performance of heat exchangers, due to the accumulation of biotic deposits with insulating characteristics in heat exchange surfaces. This accumulation adds not only an additional thermal resistance to the flow of heat but a greater frictional resistance to the passage of the fluid. The formation of these biofilms produces important modifications, since they alter the physical–chemical conditions at the metal–solution interface and form barriers for the exchange of elements between the metallic surface and the surrounding liquid medium [64]. Among the negative consequences, the decrease of the heat output of the heat exchangers and the lower durability of the construction materials of the equipment can be mentioned [65].

The main consequences produced by microfouling (biofouling) in heat exchangers are the following [5]:

- Production losses due to the decrease in efficiency and the scheduled and unscheduled shutdowns of the installation
- Maintenance costs, resulting from the elimination of biofouling deposits with chemical and/or mechanical devices
- Increased corrosion processes in metallic components, induced by microbiological corrosion (MIC) [66]
- Increased consumption of water, electricity, fossil fuels, and other sources to counteract the effects of biological fouling
- Increase in manufacturing costs of heat exchangers to consider an acceptable biological fouling without losing design power and to be able to mechanically clean them
- Increase in environmental risks due to the use of biocides and CO₂ emissions to the environment to counteract biological fouling

The main consequences of macrofouling in a heat exchanger are [40]:

- High costs caused by the complexity of the cleaning of the macroorganisms of the installation
- Losses of power produced by the loss of flow and thermal efficiency in the heat exchangers of a refrigeration installation

- Costs produced by the management of the macrofouling waste after its removal from the installation
- Production of faults due to the accumulation of macroorganisms in auxiliary systems, such as valve drives, grids, pumps, instrumentation, etc.

4. Design aspects that minimize the adhesion of biofouling

The design of the heat exchanger can represent an important factor to minimize the presence of biofouling on its surfaces. The main design variables that intervene in the biofouling growth process are [27]:

- Speed of the fluid
- Composition and roughness of the support
- Temperature of the support and cooling water
- Physicochemical properties of the fluid
- Biological variables
- Geometry of fluid passage

Although it is very difficult to relate the colonization of the surface with only one of these variables, it can be affirmed that they all have their influence on the process of developing the biofilm on the surface in contact with seawater. In this way, it is recommended to maintain minimum flow rates above 0.9 ms^{-1} and use smooth surfaces and high temperatures ($>90^\circ\text{C}$). Otherwise, the presence of biofouling on the heat exchange surface is unavoidable.

5. Chemical antifouling treatments

The chemical compounds used as antifouling agents in heat exchangers are called biocides. In addition, sequestrants, dispersants, or chelators can be used for other purposes (**Table 1**).

The biocides contain one or more active substances, whose function is to destroy, counteract, neutralize, and impede the action or exert a control of another type on any harmful organism by chemical or biological means. Properly dosed reduce drastically the number and activity of cells and biofilms in water. Due to its toxic nature, inadequate doses can be harmful to the environment and are therefore

Agent	Methodology
Sequester	Form a chemical complex with the tank keeping it in suspension
Dispersant	It transmits load to the surface keeping the particles in suspension
Chelator	It forms a strong chemical complex with the species that form the encrustation
Biocide	Kills or incapacitates generating irreversible damage to the structure or vital functions of microorganisms

Table 1.
Chemical agents used in the treatment of seawater [56].

Biocide	Ionic character	pH	Optimal activity
Cl ₂ gas	No	5–7.5	Algae and bacteria
NaClO	Anionic	7–8.5	Algae and bacterias
Br ₂	No	5–9	Algae and bacteria
ClO ₂	No	6–10	Algae, bacteria, fungi, and sulfate reducing bacteria
Chlorophenols	Anionic	5–8	Algae, bacteria, and fungi
Sales de NH ₄ ⁺	Cationic	7–9.5	Algae and bacteria
Sulfur organ	Anionic	5–7.5	Bacteria and fungi
Brominated organ	No	5–8	Algae, bacteria, fungi and sulfate reducing bacteria
Isothiazolones	No	5–8.5	Algae, bacteria, fungi, and sulfate reducing bacteria
Glutaraldehyde	No	5–8.5	Algae, bacteria, fungi, and sulfate reducing bacteria

Table 2.
Specific operating conditions of different biocides [67].

Common name	Compound
BNP	2-Bromo-2-nitro propane-1,3-diol
BNS	Beta-bromo-beta-nitrostyrene
Carbamates	Sodium dimethyl dithiocarbamate, ethylene bis dithiocarbamate disodium, disodium cyanodithioimidocarbamate, Potassium N-methyl dithiocarbamate, potassium methyl dithiocarbamate
Chlorine	Sodium hypochlorite, calcium hypochlorite trichloroisocyanuric acid, sodium dichloroisocyanide and potassium acid dichloroisocyanide
Chlorophenols	Sodium pentachlorophenate and sodium trichlorophenate
Dazomet	Tetrahydro-3,5-dimethyl-1,2-H-1,3,5-thiadiazine-2-thione
DBNPA	2,2-Dibromo-3-nitrile-propionide
DGH	Dodecylguanidine hydrochloride
Isothiazolone	5-Chloro-2-methyl-4-isothiazolon-3-one
Glutaraldehyde	1,5-Pentadial
HPMTS	Hydroxypropyl methanethiosulfonate
Hydantoin	1-Bromo-3-chloro-5,5-dimethylhydantoin, 1,3 dichloro-5,5 dimethyl hydantoin, 1,3-dichloro-5-ethyl-5-ethylhydantoin
MBT	Methylene-bis- (thiocyanate)
Sodium bromide	Sodium bromide
Sulfone	Bis- (trichloromethyl) -sulfone
TBTO	Bis- (tri-n-butyl) tin oxide
TCMTB	2(Tiocianatometiltio) benzotiazol
Triacin	Dimethyl propyl-n-ethyl-6- (methylthio) triazine diamine Chloro-4-ethylamino-6-t-butylamino-s-triazine
Tris-nitro	Tris (hydroxymethyl) nitro methane
Quaternary ammonium chloride	Didecyl dimethyl ammonium chloride, n-alkyl dimethyl benzyl ammonium chloride, dialkyl dimethyl ammonium chloride poly oxyethylene (dimethyl ammonium), ethylene (dimethylammonium) ethylene dichloride

Table 3.
Biocides used in cooling water [71].

subject to strict regulations of use [10]. These rules are increasingly restrictive, so that the situation can be reached and that the concentration of allowed biocide is lower than the effective, which requires the search for other alternatives.

Biocides used in industrial refrigeration systems must have a broad spectrum, as they must limit the growth of a wide variety of microorganisms including bacteria, fungi, and algae. In addition, they must be effective in a wide range of specific conditions of equipment operation (**Table 2**).

There is a wide variety of chemical products that have been used as biocides to inhibit the formation of biofouling deposits in heat exchange systems that use seawater as a cooling fluid. According to their general principle of action, they are classified as oxidants or as non-oxidants.

They act by oxidizing the organic matter (cellular matter, enzymes, proteins, etc.) of the microorganism, and as a consequence they cause its death [68]. Its use is widespread, and its effectiveness as a widely demonstrated antifouling agent [69, 70].

In industrial refrigeration systems, different chemical compounds are employed that have the function of drastically reducing the number of cells present in the seawater-surface interface of heat exchange and minimizing their activity, having the capacity to limit the growth of a wide variety of microorganisms (bacteria and algae) and to be effective in a wide range of equipment operating conditions (**Table 3**).

6. Biological treatments antifouling

Biological antifouling biocides are active principles created by the agencies themselves (algae, bacteria, fungi, etc.) as self-defense against other organisms in their natural environment. These substances are usually of a protein nature and are called enzymes.

Biological biocides are in the initial phase of research and development. Its use requires an in-depth analysis of the organisms that are intended to be eliminated and the environment in which they are found. The most recent research has shown the inhibition of marine biofouling by different types of bacteria, cyanobacteria, and marine fungi. Recent experiments have shown the antifouling properties of some organic compounds [72, 73], marine larvae of epibiotic bacteria [74–76], and various natural chemical compounds [77]. Dobretsov et al. [78] studied the microbial interference as a mechanism to control marine biofilms, focusing on the mechanisms of altering the biofilm by bacteria, algae, and various larvae.

7. Physical antifouling treatments

They represent an alternative to the use of biocides and an emerging research channel. They can be applied with the installation in operation (online systems) or with the installation in technical stop (offline systems) [5].

7.1 Online systems

7.1.1 Taprogge system

Mechanical cleaning system by sponge balls or elastomer material abrasives is a biofouling treatment which periodically introduce balls by the water flow to clean tubes in heat exchangers. The balls of suitable roughness are introduced into the water box of the condenser from where they pass into the tubes. Balls have a diameter greater than that of the tube which pass through tubes to clean inner surface avoiding the settlement of organic or inorganic matter.

7.1.2 Cleaning brush system housed in baskets

At the ends of the tubes, there are baskets containing a brush that moves in both directions through the interior of the tube by reversing the flow of the cooling water. The investment of flow is made with a valve system that enables this action, not being necessary more than three daily cycles to maintain good conditions of the plant.

7.1.3 Heat treatment

It consists of heating the cooling water by recirculating it in a closed circuit without renewing cold water or by installing a secondary hot water supply circuit from an internal combustion engine, for example. The water recirculates until reaching temperatures between 50 and 70°C, which produces the death of microorganisms [5]. The periodicity of this treatment is established taking into account the biological activity of the water. Its effectiveness depends mainly on the temperature of the water, the time of exposure, and the frequency of repetition [40].

7.1.4 Variation in cooling water flow rate

The speed of water flow through the tubes of the exchanger is a determining factor in the growth of biofouling. In addition to influencing the contribution of nutrients that determine the growth of organic matter that is part of the biofouling film, deposits adhered to the inner surface of the tubes can be detached as a result of the greater cutting effect on the surface are exerted to higher water flow rates. The heat exchanger can be designed to work at high flow rates (from 1 to 2 ms⁻¹) or so that the water flow rate can be varied for a short period of time (e.g., from 1 to 3 ms⁻¹) at regular intervals. This increase in flow velocity is only possible if the pumping capacity of the system can be increased.

Pulsed injections can also be made by introducing a gas (compressed air or nitrogen) at very high speed (3 ms⁻¹) periodically at short intervals of time (5, 10, and 60 minutes). The effect is to increase the turbulent regime, creating pressure fluctuations inside the tube and higher shear stresses on the surface. As a consequence, a greater detachment of biofouling is obtained than that obtained by simply increasing the speed of water flow [5]. However, according to Mussalli and Tsou [79], the effectiveness of this system decreases as the biofouling film becomes more compact.

7.1.5 Streams current antifouling

The principle of operation of this system is based on the generation of a voltage between the copper anodes (Cu) and the integrated steel cathodic plates so that when the Cu dissolves, the medium is contaminated by repelling the marine organisms. The level of Cu dissolution is regulated by a control unit adapting the system to the factors that influence biofouling growth (e.g., the season of the year) and lengthening its useful life.

7.1.6 Ultraviolet radiation

The sterilization of water by ultraviolet radiation (UV) is a potentially useful method to avoid the formation of the biofouling film and as a cleaning technique. Its principle of operation is based on attacking the deoxyribonucleic acid (DNA) of the cells, causing their death. In this way, the amount of microorganisms present in the cooling water flow is minimized.

This treatment is very effective against microorganisms in the larval stage, and their environmental impact is zero [5]. On the contrary, the useful life of UV lamps is limited (approximately 8 months), and the cost of operation and maintenance is high, which is why it is not normally used in industrial installations that require a large flow of water to treat [79].

In order to reduce the treatment and broaden the spectrum of organisms attacked, it is usually combined with another chemical or physical method [5].

7.1.7 Ultrasound

These are acoustic waves whose mode of action is based on the creation of vibrations to generate cavitation bubbles. The size of the bubbles can be increased by means of compression-decompression cycles until reaching a critical value at which they explode transforming their energy into heat. These microexplosions produce a disturbance in the surface that breaks the cohesion forces of the deposits to the surface causing their detachment [5]. Inside the cavitation bubbles, the temperature and pressure conditions can reach 5000°C and 500–2500 bar [80, 81], so that even water molecules decompose generating HO⁻ and H⁺ radicals. The radicals formed can be recombined in the same way or react with substances present in the medium causing their degradation. Obviously, the generation of radicals is facilitated if in the medium there are molecules that break easily, such as ozone or hydrogen peroxide, which also act as usual precursors of hydroxyl radicals in the oxidation processes. The greater the effectiveness of ultrasound treatments, the higher their frequency (100 Hz and 100 MHz).

This antifouling treatment is effective against microorganisms in the larval stage and also has no environmental impact. On the contrary, the high cost of the ultrasonic units must be added to the energy cost of the installation.

7.1.8 Filtering systems

These systems are considered complementary methods for the elimination of biofouling in any industrial facility. The filtrate prevents larvae of mussels, crustaceans, and other organisms from entering the circuits of refrigeration systems and therefore develops into a biofouling film.

In cooling water conduction systems, the most commonly used filters are of the panel type for flow rates of less than 10 m³ s⁻¹ and of the drum type for higher flow rates [40]. Before the installation, the overall cost/benefit of the system must be analyzed due to the pressure drop produced in the installation [79].

7.1.9 Injection of fresh water in seawater systems

The microorganisms present in the biofilm feed on the nutrients existing in the water through osmotic processes through a semipermeable membrane. When injecting fresh water, the saline concentration of the water is modified, and the pressure inside the cells increases, causing death [5]. According to Cho et al. [82], the exposure time must be high, reaching 48 hours for the mussel *Mytilus californianus* and 63 hours for the mussel *Mytilus edulis*. This method is used in piping systems of refrigeration systems that remain out of service for long periods [83].

7.1.10 Inserts in the tubes

This system consists of inserting a helical element, whose vibration, distortion of flow, or rotation mitigate the growth of biofouling adhering on the inner surface of the tubes [5].

This system can present the following variants [84]:

- SPIRELF®. Metallic helical element attached to the ends of the tube and adjusted to its length. When the fluid circulates inside the tube, it vibrates axially and radially, eliminating biofouling adhering to its walls.
- FIXOTAL® or HITRAN®. They use metallic helical elements that are fixed inside the tubes, improving the turbulent effect on the wall to reduce the thickness of biofouling.
- TURBOTAL®. Rigid helical device that is inserted into the tubes and uses the water flow itself as the impeller of the rotating cleaning mechanism.

The insertion of metal elements inside the tubes has proven to be an effective method to prevent the formation of biofouling in heat exchangers of different industrial processes [84]. However, the use of this type of device means increasing the cost of the equipment and its maintenance, as well as a higher consumption of pumping energy due to the increase of load losses in the system.

7.1.11 Circulation of polymers

The method consists of introducing polymer fibers entrained by the fluid stream in order to erode and detach the layer of adhered deposits. According to Bott [5], its effectiveness on the process of forming the biofouling film in the tubes of a heat exchanger depends on the concentration of fibers and the speed of the flow of cooling water. The biggest drawback is that of removing the fibers from the effluent before it is discharged into the natural environment.

7.1.12 Treatments with electromagnetic fields

Electromagnetic fields have the ability to increase the interaction of the Ca^{2+} and CO_3^{2-} ions present in seawater, increasing their nucleation and precipitation in CaCO_3 . Below 35°C , CaCO_3 precipitates in the form of aragonite instead of calcite, resulting in being less adherent and less insulating [3, 85, 86]. The precipitation process of CaCO_3 reduces the superficial tension of the water, minimizing the adherence of microorganisms, and affects the intermolecular union of the extracellular polymers, weakening the matrix of the biofouling layer and diminishing its capacity of adhesion to the surface [7]. In addition, CaCO_3 entrainment by the seawater flow produces an erosive effect on the weakened biofouling layer that reduces its thickness [87, 88].

7.2 Offline systems

The use of online antifouling treatments does not prevent periodically scheduled stops in which aggressive cleaning methods are used to recover the efficiency of the tube at 100%. The frequency of scheduled stops is based on experience, and the cost/benefit ratio is derived from its application.

Brushing the surfaces of the heat exchanger in a dry or wet surface condition to eliminate adhering deposits. The cost of cleaning is high and involves access to the surfaces of the exchanger.

Although the techniques used to clean the surfaces of an industrial heat exchanger are varied, the most common methods to clean the internal surface of the pipes are air, water, and water steam.

The choice of cleaning agent depends on the degree of adhesion of the tanks and the design of the heat exchanger. According to Wilson [89], the use given to the different cleaning agents is as follows:

- Air under pressure. Eliminates deposits that are not very adherent
- Water at high pressure. Eliminates deposits and calcium deposits in tubular exchangers, condensers, and low-pressure boilers
- Water vapor. Eliminates calcareous incrustations and other substances of great hardness

To increase cleaning efficiency, detergents or abrasive materials are added to water or air under pressure. The nature of the abrasive materials depends on the hardness of the tanks and the construction material of the equipment. Sand is used as abrasive materials, pulverized mollusk shells, etc. [89].

8. Conclusions

Nowadays, heat exchangers play a vital role in the operational efficiency and effectiveness at every processing facility in which heat is essential, whether it is an oil refinery, combined heat and power plants, solar and biomass power plant, etc. As energy efficiency importance grows, the role of heat exchangers will become even greater and their technologies more advanced. Fouling on heat transfer surfaces of power plants are a major economic and environmental problem worldwide. Estimates have been made of fouling costs due primarily to wasted energy through excess fuel burn that are as high as 0.25% of the gross national product (GNP) of the industrialized countries. Many millions of tons of carbon emissions are the result of antifouling inefficiency.

After this study of the state of the art of fouling in heat exchanger, the main conclusion is that fouling problem is latent and unresolved. For this reason, new research projects must be developed to investigate and resolve this old problem without environmental effect.

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